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Dr. Ahmed H. Zewail

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California Institute of Technology — 1200 East California Blvd., M/C 127-72, Pasadena, CA 91125

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14. ABSTRACT

We proposed to use this grant to undertake research in the following three major areas:

(a) Dynamics of elementary steps in complex systems.
(b) Dynamics of reactions under extreme environment (density, temperature, clustering, etc.).
(c) New techniques for direct imaging of structural changes and chemical control of reactions yield and channel.

In these studies, the basic approach is based on the development of ultrafast laser (and electron) and molecular beam techniques to examine in real time the nature of the dynamics and structures on the femtosecond time scale. Our goal was to relate these dynamics to features of bonding and mechanisms and to explore the effect of extreme solvation environment on reactivity. Probing and controlling reactions pathways are key to validating any model of chemical reactivity in complex molecular systems. Theoretical studies in our group and in collaboration with colleagues elsewhere were an important part of

15. SUBJECT TERMS

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Final Performance Report

Air Force Office of Scientific Research

AFOSR Grant No. F49620-98-1-0059

"Femtosecond Dynamics of Chemical Reactions"

Ahmed H. Zewail, Principal Investigator

California Institute of Technology

Division of Chemistry and Chemical Engineering
Mail Code 127-72
1200 East California Boulevard
Pasadena, California 91125

March 29, 2004

OBJECTIVES

We proposed to use this renewal grant to undertake research in the following three major areas:

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(b) dynamics of reactions under extreme environment (density, temperature, clustering, etc.)

(c) new techniques for direct imaging of structural changes and chemical control of reactions yield and channel.

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STATUS OF EFFORT

We have made significant progress in several areas (please see below and the publication list), including the development of UED for imaging and studying the dynamics of molecular systems with *atomic-scale* resolution, and the dynamics of elementary processes in complex reactions, including ionic systems. The Caltech group has so far published papers in every category, as outlined below.

ACCOMPLISHMENTS/NEW FINDINGS

Our accomplishments and new findings are in three areas: (a) fundamental R/D; (b) new technologies and techniques; and (c) education and training of research associates at Caltech.

In the area of fundamental R/D, we have made the following specific accomplishments, highlighted in the summary given below:

(1) Ultrafast Electron Diffraction

With properly timed sequences of ultrafast electron pulses, it is now possible to image complex molecular structures in the four dimensions of space and time with resolutions of 0.01 Å and 1ps, respectively. The new limits of ultrafast electron diffraction (UED) provide the means for the determination of transient molecular structures, including reactive intermediates and non-equilibrium structures of complex energy landscapes. By freezing structures on the ultrafast timescale, we are able to develop concepts that correlate *structure* with *dynamics*. Examples include structure-driven radiationless processes, dynamics-driven reaction stereochemistry, pseudorotary transition-state structures, and non-equilibrium structures exhibiting negative temperature, bifurcation, or selective energy localization in bonds. These successes in the studies of complex molecular systems, even without heavy atoms, and the recent development of a new machine devoted to structures in the condensed phase, establish UED as a powerful method for mapping out temporally changing molecular structures in chemistry, and potentially, in biology. A recent review* highlights the advances made at Caltech, with emphasis on the principles of UED, its evolution through four generations of instrumentation (UED-1 to UED-4) and its diverse applications. [*Ultrafast Electron Diffraction (UED) A New Development for the 4D Determination of Tansient Molecular Structures, Ramesh Srinivasan, Vladimir A. Lobastov, Chong-Yu Ruan, and A. H.

Zewail, Review Article, *Helvetica Chimica Acta.*, **86**, 1761-1838 June Special Issue, 1 (2003).]

(2) Microscopic Solvation

Ultrafast dissociation and recombination dynamics of $(O_2)_n^-$, $n=3-10$ was studied using femtosecond, time-resolved photoelectron spectroscopy. The observed transients of nascent fragment anions, following 800 nm fs pulse excitation, exhibit a biexponential rise with two distinct time constants. The time constants, which vary with the number of solvent O_2 molecules, clearly show the solvation effect in two different dissociation pathways. Consistent with the bifurcation picture in the preceding paper, the direct subpicosecond dissociation ($\tau_1 = 110-620$ fs, depending on n) is governed by electron recombination and kinematics of the half-collision. The second pathway is indirect ($\tau_2 = 0.7-8.0 ps$, for O_6^- to O_{20}^-) and controlled by intramolecular vibrational-energy redistribution. In the solvent cage, only O_{16}^-, O_{18}^-, and O_{20}^- show the reformation of the bond, with the caging time constant decreasing from 4 ps for the first two to 2 ps for the latter. This caging through ion-induced dipole interaction is then followed by vibrational relaxation on the time scale of 12 to 3 ps, for O_{16}^- to O_{20}^-. The time scale for the initial direct caging is two to five times slower than that previously observed for diatoms, neutral, or ionic, in van der Waals clusters. We showed that this initial slower caging is due to the reorientation of O_2^- and O_2 to acquire a proper geometry for O_4^- bond reformation. In these finite-sized homogeneous clusters, we compared theory with experiment. We also found a correlation between the vertical detachment energy and $n^{-1/3}$, for n in the range of 2-10, which allow for a connection between the mesoscopic structures and a bulk-type dielectric continuum, with an effective dielectric constant. These types of studies are critical to our understanding of energy disposal in complex systems.* [*Femtosecond dynamics of solvated oxygen anions. II. Nature of

dissociation and caging in finite-sized clusters, Nam Joon Kim, D. Hern Paik, and A. H. Zewail, *J. Chem. Phys.* **118**, 6930 (2003).]

Finally, the Caltech group currently has close to 30 visiting associates, post-doctoral fellows, graduate students and undergraduate students. The training and education of a new generation of scientists and technologists in these areas has been extremely profitable, as evident by the leading positions these associates acquire in academic institutions and in the industrial sector.

PERSONNEL SUPPORTED

Several graduate students and post-doctoral research fellows have been involved (supported, partially supported, or having their own fellowships) in this research. Over the years, many from this group have been successful in obtaining leading positions, and the list includes:

Dr. P. Felker (presently on the faculty at UCLA)
Dr. M. Gruebele (presently on the faculty at the University of Illinois at Urbana-Champaign)
Dr. M. Dantus (presently on the faculty at Michigan State University)
Dr. W. Warren (presently on the faculty at Princeton University)
Dr. N. Scherer (presently on the faculty at the University of Chicago)
Dr. J. Perry (presently on the faculty at Georgia Tech)
Dr. D. Millar (presently on the faculty at Scripps)
Dr. J. Knee (presently on the faculty at Wesleyan University)
Dr. R. Bowman (presently on the faculty at Colgate University)
Dr. L. Bañares (presently on the faculty at Complutense de Madrid University)
Dr. G. Roberts (presently at the University of Cambridge)
Dr. M. Janssen (presently at the University of Amsterdam)
Dr. M. Rosker (presently at Rockwell)
Dr. T. Rose (presently at Aerospace Corporation)
Dr. T. Baumert (presently on the faculty at University of Kassell)
Dr. J. Cao (presently on the faculty at Florida State University)
Dr. A. Douhal (presently on the faculty at Universidad de

Castilla-La Mancha
Dr. Eric Wei-Guang Diau (presently on the faculty at National Chiao-Tung University, Taiwan)
Dr. Arnulf Materny (presently on the faculty of the International University Bremen)
Dr. Boyd Goodson (presently on the faculty at Southern Illinois U.)
Dr. Hyotcherl Ihee (presently on the faculty at KAIST, Korea)
Dr. Nam Joon Kim (presently on the faculty at Chungbuk National University, Korea)
Dr. Carsten Kötting (presently on the faculty at Ruhr-Universität Bochum, Germany)
Dr. Jorge Peon-Peralta (presently on the faculty at the University of Mexico)
Dr. Xiaogang Qu (presently on the faculty of the Chinese Academy of Sciences)
Dr. Theis Sølling (presently at the University of Copenhagen, Denmark)
Dr. Dongping Zhong (presently on the faculty at Ohio State University)
Dr. Shouzong Zou (presently on the faculty at Miami U. in Ohio)
Dr. Samir Pal (presently on the faculty of the Bose Institute in Calcutta in the fall of 2003)
Dr. Hans-Christian Becker (presently on the faculty of Uppsala University, Sweden)
Dr. Qing-Bin Lu (presently on the faculty at the University of Waterloo, Canada)
Dr. Chong-Yu Ruan (presently on the faculty at Michigan State University)

At Caltech, current **postdoctoral research fellows** are: S. Baskin, M. D'Orsogna, A. Kamal, V. Lobastov, S.T. Park, C.-Y. Ruan, F. Vigliotti, C. Wan, Y. Wang, T. Xia, S. Xu, and L. Zhao. Current **graduate students** are: S. Chen, F. J. Feenstra, I.-R. Lee, H. Paik, R. Srinivasan, D. Yang, and L. Zhang.

In addition, we have had collaborative efforts with Professors J. Barton, F. Anson, W. Goddard, V. McKoy, R. Roberts, Z.-G. Wang (Caltech); Professor K. Houk (UCLA); Professor A. Scala (Worcester Polytechnic Institute, Massachusetts); Professor J. Casanova (California State University, Los Angeles); and Professor Gustav Gerber (University of Würzburg).

PUBLICATIONS - Articles (selected publications)

Direct Determination of Hydrogen-Bonded Structures in Resonant and Tautomeric Reactions Using Ultrafast Electron Diffraction

Ramesh Srinivasan, Jonathan S. Feenstra, Sang Tae Park, Shoujun Xu, and A. H. Zewail
J. Am. Chem. Soc., **126**, 2266-2267 (2004)

Ultrafast Electron Diffraction and Transient Complex Structures: From Gas Phase to Crystallography

A. H. Zewail
Femtochemistry and Femtobiology: Ultrafast Events in Molecular Science,
Ed. M. Martin and J.T. Hynes, Elsevier, (2004)

Ultrafast Electron Diffraction. From the Gas Phase to the Condensed Phase with Picosecond and Femtosecond Resolution

Vladimir A. Lobastov, Ramesh Srinivasan, Franco Vigliotti, Chong-Yu Ruan, Jonathan S. Feenstra, Songye Chen, Sang T. Park, Shoujun Xu, and A. H. Zewail
Springer Series in Optical Sciences, Ed. Krausz, F. (2003).

Femtosecond Dynamics of Solvated Oxygen Anions: I. Bifurcated Electron Transfer Dynamics Probed by Photoelectron Spectroscopy

D. Hern Paik, Nam Joon Kim, and A. H. Zewail
J. Chem. Phys. **118**, 6923 (2003)

Femtosecond Dynamics of Solvated Oxygen Anions: II. Nature of Dissociation and Caging in Finite-Sized Clusters

Nam Joon Kim, D. Hern Paik, and A. H. Zewail
J. Chem. Phys. **118**, 6930 (2003)

Ultrafast Electron Diffraction: Complex Landscapes of Molecular Structures in Thermal and Light-Mediated Reactions

Boyd M. Goodson, Chong-Yu Ruan, Vladimir A. Lobastov, Ramesh Srinivasan, and A. H. Zewail
Chem. Phys. Lett, **374**, 417-424 (2003)

Ultrafast Electron Diffraction (UED) A New Development for the 4D Determination of Transient Molecular Structures

Ramesh Srinivasan, Vladimir A. Lobastov, Chong-Yu Ruan, and A. H. Zewail
Review Article
Helvetica Chimica Acta. June Special Issue, 1 (2003)

Orientation Dynamics and Molecular Structures from Gas Phase to Condensed Media.

J.S. Baskin and A.H. Zewail
in: *Femtochemistry and Femtobiology: Ultrafast Dynamics in Molecular Science*
ed. A. Douhal and J. Santamaria (World Scientific, Singapore, 2002)

Ultrafast Electron Diffraction of Transient Cyclopentadienyl Radical: A Dynamic Pseudorotary Structure

H. Ihee, J.S. Feenstra, J. Cao, and A.H. Zewail
Chem. Phys. Lett. **353**, 325-334 (2002)

Ultrafast Electron Diffraction and Structural Dynamics: Transient Intermediates in the Elimination Reaction of $C_2F_4I_2$

H. Ihee, B.M. Goodson, R. Srinivasan, V.A. Lobastov, and A.H. Zewail
J. Phys. Chem. A, **106**, 4087 (2002)

Kinetics Modeling of Dynamics: The Case of Femtosecond-Activated Direct Reactions

K.B. Møller and A.H. Zewail
Chem. Phys. Lett. **351**, 281-288 (2002)

Coherent Dynamics in Complex Elimination Reactions: Experimental and Theoretical Femtochemistry of 1,3-Dibromopropane and Related Systems

C. Kötting, Eric W.-G. Diau, T.I. Sølling and A.H. Zewail
J. Phys. Chem. A, **106**, 7530 (2002)

Chemistry at the Uncertainty Limit

A.H. Zewail
Angew. Chem. **40/23**, 4371 (2001)
Angew. Chem. Int. Ed. (German) **113/23**, 4501 (2001)

Ultrafast Diffraction of Transient Molecular Structures in Radiationless Transitions

V.A. Lobastov, R. Srinivasan, B.M. Goodson, C.-Y. Ruan, J.S. Feenstra and A.H. Zewail
J. Phys. Chem. A. **105**, 11159 (2001)

Femtochemistry of Norrish Type-I Reactions: IV. Highly-Excited Ketones, Experimental

T.I. Sølling, E. W.-G. Diau, C. Kötting, S. De Feyter, and A.H. Zewail
Chem. Phys. Chem. **3**, 79-97 (2002)

Direct observation of resonance motion in complex elimination reactions: Femtosecond coherent dynamics in reduced space.

C. Kötting, E. W.-G. Diau, J.E. Baldwin, and A.H. Zewail
J. Phys. Chem. A **105**, 1677 (2001)

Femtochemistry of Norrish Type-I Reactions: I. Experimental and Theoretical Studies of Acetone and Related Ketones on the S_1 Surface

E. W.-G. Diau, C. Kötting, and A.H. Zewail
Chem. Phys. Chem. **2**, No. 5, 273 (2001)

CF_2XCF_2X and CF_2SCF_2.•radicals (X = Cl, Br, I): Ab Initio and DFT Studies and Comparisons with Experiments

H. Ihee, J. Kua, W.A. Goddard III, and A.H. Zewail
J. Phys. Chem. A **105**, 3623 (2001)

Direct Imaging of Transient Molecular Structures with Ultrafast Diffraction

H. Ihee, V. Lobastov, U. Gomez, B. Goodson, R. Srinivasan, C. -Y. Ruan, and A.H. Zewail
Science **291**, 385 (2001)

Femtochemistry--Atomic-Scale Dynamics of the Chemical Bond using Ultrafast Lasers, Les Prix Nobel, The Nobel Prizes, Nobel Biography, "A Personal Voyage Through Time" and Nobel Address

A.H. Zewail
Almquist & Wiksell International, Stockholm (2000) - Book Chapter;
Angewandt Chemie,, Invited, International Edition, **39**, 2586-2631 (2000); German Edition, **112**, 2688-2738 (2000)

Femtochemistry – Atomic-Scale Dynamics of the Chemical Bond

H. Zewail
J. Phys. Chem. – Feature Article (Nobel Lecture), **104**, 5660 (2000)

INTERACTIONS/TRANSITIONS

Participation/Presentations at Meetings and Conferences (Examples)

Keynote Address, Linus Pauling Centenary, Oregon State University, Corvallis, February 28, 2001

Schrödinger's Wave Mechanics (75th) Celebration Lecture, University of Zürich, Switzerland, April 24, 2001

George B. Kistiakowsky Lecture, Harvard University, Cambridge, Massachusetts, April 30, 2001

The National Institutes of Health Director's Lecture, Bethesda, Maryland, May 4, 2001

National Science Foundation Distinguished Lecture (MPS), Arlington, Virginia, May 7, 2001

Plenary Opening Lecture, Joint CLEO/QELS 2001, Conference on Lasers and Electro-Optics/Quantum Electronics and Laser Science Conference, Baltimore, Maryland, May 8, 2001

Inauguration of Lectures of Nobel Prize Winners, Public Conference, Novartis & University of Basel, Basel, Switzerland, June 12, 2001

Inauguration of La Premiere Conference Jean Perrin, Collége de France, Paris, France, June 18, 2001

Albert Einstein Lecture, New Delhi, India (2002)

Keynote Lecture, NanoBioScience Institute, South Korea (2002)

Nobel Youth Lecture, Royal Swedish Academy, Stockholm (2002)

U Thant Distinguished Lecture Series, United Nations University, Tokyo, Japan (2003)

Republic of Korea Visit: Meeting, Minister of Commerce, Industry & Energy, Seoul, April 18, 2003; Meeting, Minister of Health & Welfare, Seoul, April 17, 2003; Meeting (with presentation) CEO and two Vice Chairmen of Samsung Co., Seoul, April 17, 2003

Opening Lecture; "Ultrafast Dynamics with Diffraction and Mass Spectrometry"; Air Force Office of Scientific Research Meeting; Shelter Pointe Hotel, (San Diego, California), May 18, 2003

Keynote Address; "Voyage of Discoveries"; California State Science Fair; California Science Center, (Los Angeles, California) May 19, 2003

Opening Lecture; "Biostructures in Space and Time"; Frontiers in Chemistry, Georgia Tech College of Sciences, (Atlanta, Georgia) May 23, 2003

Opening Lecture; "Energy and Our World", Swedish Academy of Sciences Conference, (Stockholm, Sweden), March 9, 2004

Consultative and Advisory Functions (Examples)

Editor, *Chemical Physics Letters*
Advisory Editorial Board, *Chemical Physics*
Editorial Board of Advisors, *Laser Focus World*
Editorial Board,*The Chemical Intelligencer*
Advisory Board, *American Men and Women of Science*
Advisory Board, *World Scientific*

Advisory Board of the Laser Facility, University of Pennsylvania
Advisory Board, The University of Basel, Switzerland
Editorial Advisory Board, *Chemical Reviews*
Advisory Board, *Angewandte Chemie* (Chem. Phys. Chem.)
Editorial Board, Cambridge University Press Series

Transitions

Throughout the development of ultrafast imaging techniques we have exchanged the new findings on the bombardment of CCD's with electrons with the Jet Propulsion Laboratory, where these CCD technologies are an essential part of the Space Program. We have also benefited greatly from their expertise in this area. The development of UED represents major advances in the technology of ultrafast electrons, lasers, and computers.

NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

During the period of the grant we have made one major development and some new discoveries. In a paper published in *Science,* we have developed ultrafast electron diffraction to a new level. With this apparatus, for the first time, we are able to clock a change of chemical structure of *intermediates* with one picosecond resolution, and with a spatial resolution of 0.01Å. As described in a publication to appear soon in *Science,* we believe that a breakthrough in this field has been made. We are now able to perform diffraction of crystals and materials on the nanometer scale.

The discovery of a new ultrafast phenomenon in mesoscopic systems is novel and significant. In a series of publications in the journal of *Chemical Physics,* we reported on studies of oxygen anion clusters with first and second solvation shells. These are important

mesoscopic systems that are highly reactive in chemical and biological (O_2^-) systems. Other discoveries are reported in the references given.

HONORS/AWARDS (INCOMPLETE)

The Nobel Prize in Chemistry
The Ahmed Zewail Fellowships, University of Pennsylvania
Other awards are listed on the curriculum vitae, and on the web page at www.its.caltech.edu/~femto/zewail.htm

D.Sc., h.c., (honorary degree) Katholieke Universiteit, Leuven, Belgium (1997)
D.Sc., h.c., (honorary degree) University of Pennsylvania, U.S.A. (1997)
D.Sc., h.c., (honorary degree) Université de Lausanne, Switzerland (1997)
D.U., h.c., (honorary degree) Swinburne University, Australia (1998)
Doctoris in Scientia, D.Sc., h.c. (honorary degree) University of New Brunswick, Canada (2000)
Dottore *honoris causa*, D., h.c. (honorary degree) University of Rome "La Sapienza"(2000)
Doctor *honoris causa*, D., h.c. (honorary degree) Université de Liège, Belgium (2000)
Doctor *honoris causa*, D., h.c. (honorary degree) Heriot-Watt University, Scotland (2002)
D.Ph., h.c. (honorary degree) Lund University, Sweden (2003)

Member:

National Academy of Sciences
Pontifical Academy of Sciences
American Philosophical Society
The Royal Danish Academy of Sciences & Letters
American Academy of Arts and Sciences
American Philosophical Society
Académie Européenne des Sciences, des Arts et des Lettres, France
American Physical Society
American Association for the Advancement of Science
Third World Academy of Sciences, Italy
American Chemical Society
Inter-American Photochemical Society
Sigma Xi Society
Royal Society of London
Russian Academy of Sciences

Royal Swedish Academy of Sciences